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Tillage System, Application Rate, and Extreme Event Effects on Herbicide Losses in Surface Runoff

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ABSTRACT

Conservation tillage can reduce soil loss; however, the residual herbicides normally used to control weeds are often detected in surface runoff at high levels, particularly if runoff-producing storms occur shortly after application. Therefore, we measured losses of alachlor, atrazine, linuron, and metribuzin from seven small (0.45–0.79-ha) watersheds for 9 yr (1993–2001) to investigate whether a reduced-input system for corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] production with light disking, cultivation, and half-rate herbicide applications could reduce losses compared with chisel and no-till. As a percentage of application, annual losses were highest for all herbicides for no-till and similar for chisel and reduced-input. Atrazine was the most frequently detected herbicide and yearly flow-weighted concentrations exceeded the drinking water standard of 3 μg L^{-1} in 20 out of 27 watershed years that it was applied. Averaged for 9 corn yr, yearly flow-weighted atrazine concentrations were 26.3, 9.6, and 8.3 μg L^{-1} for no-till, chisel, and reduced-input, respectively. Similarly, flow-weighted concentrations of alachlor exceeded the drinking water standard of 2 μg L^{-1} in 23 out of 54 application years and in all treatments. Thus, while banding and half-rate applications as part of a reduced-input management practice reduced herbicide loss, concentrations of some herbicides may still be a concern. For all watersheds, 60 to 99% of herbicide loss was due to the five largest transport events during the 9-yr period. Thus, regardless of tillage practice, a small number of runoff events, usually shortly after herbicide application, dominated herbicide transport.

Conservation tillage practices are often used for corn and soybean production to reduce soil loss, improve soil quality, and maintain eligibility for commodity support payments. In areas with steeply sloping cropland, these crops can be grown in a 2-yr rotation with soil losses below tolerance levels if conservation tillage is used and cereal rye (*Secale cereale* L.) is planted as a winter cover following soybean to increase residue cover (Edwards et al., 1993). Herbicides and fertilizers must be used with this rotation. Unfortunately, under these conditions, herbicide (Shipitalo et al., 1997) and NO_3 (Owens and Edwards, 1993) concentrations in runoff frequently exceed established maximum contaminant levels (MCLs) for drinking water, particularly in the first few runoff events after application, and may be a concern. In fact, some research suggests that herbicide concentrations in runoff are higher with no-till than with other conservation tillage practices (Fawcett et al., 1994). A possible contributing factor to this observation is that tillage performed in conjunction with herbicide application can increase surface roughness and reduce runoff volumes in the first few storms after application, although runoff on an annual basis is greater than with conservation tillage. It is the first few storms after application, however, that are often responsible for the largest herbicide losses (Baker and Mickelson, 1994).

Best management practices that might reduce herbicide losses in surface runoff include banding and reduced-rate applications (Baker and Mickelson, 1994; Wauchope et al., 1994). Hall et al. (1972) found that herbicide losses in runoff were proportional to the application rate, which led Baker and Mickelson (1994) to speculate that banding should reduce herbicide losses by half. Subsequent modeling (Gorneau et al., 2001; Harman et al., 2004) and plot (Hansen et al., 2001) studies have shown that banding can reduce herbicide losses in runoff compared with broadcast applications. Reductions in herbicide transport and concentrations in percolate proportional to the reductions in application rate have also been observed with banded (Heydel et al., 1999) and reduced-rate applications (Hanson et al., 1997). These practices, however, may require increased tillage that can increase the risk of soil loss (Harman et al., 2004; Shipitalo and Edwards, 1998).

It is well established that pesticide transport in surface runoff is largely dependent on the timing and intensity of rainfall with respect to pesticide application (Fawcett et al., 1994; Locke and Bryson, 1997; Wauchope et al., 1994). Similarly, research has demonstrated that large, infrequent, storms produce most of the soil loss from small watersheds and plots (Edwards and Owens, 1991; Hjelmfelt et al., 1986; Langdale et al., 1992). For example, Edwards and Owens (1991) noted that during a 28-yr period, an average of 25% of the soil loss from nine moldboard-plowed watersheds in a 4-yr corn–wheat (*Triticum aestivum* L.)–meadow–meadow rotation was due to the single largest erosion-producing event. With an average of 4000 rainfall events during this period, the five largest events produced an average of 66% of the soil loss. They concluded that long-term records are necessary to quantify the effects of rare, big events. Larson et al. (1997) further concluded that conservation practices must be designed to control erosion from severe storms to be effective. A similar analysis of the long-term effects of conservation tillage practices on herbicide losses has yet to be conducted. While the occurrence of rainfall cannot

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Abbreviations: DAA, days after application; HAL, health advisory level; MCL, maximum contaminant level; NAEW, North Appalachian Experimental Watershed.

be controlled, such information would be useful in highlighting the importance of extreme events and could prompt development of management practices that mitigate their effects.

Therefore, our objective was to evaluate the effects of three conservation tillage practices (no-till, chisel-till, and reduced input) on herbicide transport and concentrations in surface runoff. Banding and half-rate herbicide applications were part of the reduced-input practice to determine if these practices could reduce herbicide losses and concentrations to acceptable levels while keeping erosion below the soil loss tolerance value. The study was conducted for 9 yr so that the long-term effect of these conservation practices and infrequent, extreme events could be evaluated.

MATERIALS AND METHODS

Watershed Management

Losses of alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl) acetamide], atrazine (2-chloro-4-ethylamine-6-isopropylamino-*S*-triazine), linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea], and metribuzin [4-amino-6 (1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one] in surface runoff from two no-till and two chisel-tilled watersheds in a 2-yr corn–soybean rotation and three disked watersheds in a 3-yr, reduced-input, corn–soybean–wheat–red clover (*Trifolium pratense* L.) rotation were monitored year-round for 9 yr (spring 1993–spring 2002). A cereal rye cover crop was either broadcast seeded or drilled into the soybean residue after harvest in September or October in the no-till and chiseled watersheds. With the reduced-input watersheds, winter wheat was drilled into the soybean residue in October following harvest and red clover was broadcast seeded into the standing wheat the following March or April. After wheat harvest in July, the red clover was allowed to grow until the next spring, when it was disked into the soil along with 4 to 9 Mg ha^{-1} of high-straw cattle manure to supply most of the N needed by the following corn crop.

One watershed in each tillage treatment was planted to each crop each year. All seven watersheds are within 1 km of each other and are part of the network of watersheds maintained by the USDA-ARS for >60 yr at the North Appalachian Experimental Watershed (NAEW) near Coshocton, OH. Weighing-type rain gauges positioned near each watershed were used to record precipitation amounts and intensities. General characteristics and tillage treatments of the watersheds are outlined in Table 1. Detailed information on the soil properties and soil distribution within the watersheds is available in Kelley et al. (1975). Tillage treatments were not randomized, but were assigned to the watersheds based on long-term hydrologic records, with one watershed in each tillage treatment having a history of less than average runoff production. Consequently, statistical comparisons among tillage treatments were not performed.

A chisel plow with straight shanks at a 30-cm spacing was used to till the chisel watersheds to a depth of 25 cm shortly before planting corn or soybean. No secondary tillage operations were conducted on these watersheds. The reduced-input watersheds were disked to a depth of ~10 cm three to four times before planting in corn and soybean years. This light, shallow, disking was designed to leave some of the residue cover intact and to confine and concentrate the buried residue near the soil surface to minimize the adverse effects of residue incorporation observed with moldboard plowing. These watersheds were usually cultivated between the rows once in June and once in July for additional weed control in corn and soybean years. Corn was planted at 76-cm row spacing on all watersheds and soybean was planted at this spacing on the reduced-input watersheds to allow for cultivation. Soybean was planted at 18-cm spacing on the remaining watersheds.

Table 1. Tillage treatments and characteristics of the seven watersheds.

Watershed	Tillage treatment	Area	Avg. slope	Max. length	Dominant soil series†
		ha	%	m	
WS 109‡	chiseled	0.68	13	110	Rayne silt loam
WS 123	chiseled	0.55	7	107	Keene silt loam
WS 113‡	no-till	0.59	11	118	Coshocton silt loam
WS 118	no-till	0.79	10	132	Coshocton silt loam
WS 111	disked	0.45	6	143	Keene silt loam
WS 115‡	disked	0.65	7	119	Coshocton silt loam
WS 127	disked	0.67	9	104	Coshocton silt loam

† Taxonomic classification: Rayne–fine-loamy, mixed, active, mesic Typic Hapludult; Keene–fine-silty, mixed, superactive, mesic Aquic Hapludalf; Coshocton–fine-loamy, mixed, active, mesic Aquultic Hapludalf.
‡ Low-runoff-producing watershed based on historical records.

Weed control on the chisel-tilled and no-till watersheds was achieved by broadcast application of 3.36 kg ha^{-1} alachlor, 2.24 kg ha^{-1} atrazine, and 1.12 kg ha^{-1} linuron in corn years and 3.36 kg ha^{-1} alachlor and 0.38 kg ha^{-1} metribuzin in soybean years shortly after planting. A half-rate broadcast application of herbicide was used on the reduced-input watersheds when sown to corn. Herbicide was applied only to a 38-cm-wide band over the row when soybean was planted, which resulted in half-rate application on a per-hectare basis. The herbicides were not incorporated during application and all tillage and planting operations were performed along the contour of the watersheds. The crop and tillage management practices on the watersheds were identical to those during the study for a minimum of 3 yr before the beginning of the experiment. The timing of all field operations coincided with the standard practices used for the production of these crops in Ohio.

Sampling Methodology

Runoff volumes were measured using H flumes housed within enclosures that permitted year-round operation of the watersheds (Brakensiek et al., 1979). Data loggers were used to record the hydrographs and activate Isco samplers (Teledyne Isco, Lincoln, NE) equipped with stainless steel strainers, Teflon suction lines, and glass sample bottles. Up to 28 samples per watershed were obtained each time runoff occurred. During runoff, the samplers collected discrete samples (~300 mL) every 10 min for the first 100 min, every 20 min for the next 200 min, and every 60 min thereafter until the capacity of the samplers was reached or runoff ceased. Samples were brought in from the field and refrigerated usually shortly after runoff ceased and, in most instances, did not remain in the samplers longer than overnight.

Generally, at the beginning of the crop year, all collected samples were analyzed. As herbicide concentrations in the runoff declined during the year, only samples representative of the beginning, peak, and tail of the hydrograph of each event were analyzed. Flow-weighted average concentrations for each runoff event were computed using the concentrations measured in individual samples and runoff volumes obtained from the hydrographs. When runoff occurred for a prolonged period of time in the winter and early spring, and in instances when the automated samplers failed to operate properly, flow-proportional composite samples were obtained using Coshocton wheels (Brakensiek et al., 1979).

Analytical Procedures

Herbicides were extracted from unfiltered runoff samples using LC-18 solid-phase extraction tubes. Internal standards propachlor (2′-chloro-*N*-isopropyl acetanilide) and oxadiazon [2-tert-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)- Δ^2-2-1,3,4-oxadiazolin-5-one] were added to the prepared extracts and they were analyzed using a gas chromatograph equipped with an autosampler, a temperature-programmable on-column injector, and a thermionic-specific detector. Each sample was run on two capillary columns of dissimilar polarity (Penton, 1991). When the concentrations differed, the lower value was used on the assumption that the higher value was due to positive interference by other compounds, thus the estimated losses are conservative. The amount of sample extracted increased from 1 to 40 mL as herbicide concentrations decreased with time after application. The minimum detection limits were: atrazine, 0.03 μg L^{-1}; metribuzin, 0.06 μg L^{-1}; alachlor and linuron, 0.13 μg L^{-1}.

RESULTS

General Observations

The timing of field operations varied from year to year as dictated by weather conditions. In an individual crop year, however, herbicide applications to the no-till and chisel-tilled watersheds were made on the same date, whereas the date of application on the disked watersheds was somewhat delayed in most years to allow for extra time and suitable soil conditions necessary to complete the additional tillage operations these watersheds received. Therefore, to make comparisons among tillage treatments and years, the crop year was defined as beginning on the day of herbicide application and ending with herbicide application the following year. In the case of the wheat–red clover years, when herbicides were not applied, the crop year was assumed to begin on 1 June. Consequently, variations in precipitation totals among watersheds within years (Table 2) were attributable to variations in crop year ending and starting dates as well as slight differences in actual precipitation at each site.

Precipitation measured in this fashion ranged from 840 to 1165 mm per crop year and the precipitation averages for the 9-yr period for the three tillage treatments were quite similar (chisel-tilled, 953 mm; no-till, 976 mm; disked, 960 mm). These averages approximated the long-term (1937–2004) average precipitation observed at the NAEW of 958 mm yr^{-1}. Thus, although a wide range of weather years were encountered during the study, the experiment spanned enough years to yield near-average precipitation. The amount of surface runoff generated by this precipitation varied among watersheds and years. Except in 2000 with the reduced-input treatment, the watersheds identified a priori as low-runoff-producing yielded a smaller percentage of precipitation as runoff than the other watersheds in the corresponding tillage treatment (Table 2). This reflects the unique soil and topographic characteristics of the watersheds that can have an overriding effect on runoff production.

A total of 1697 separate runoff events were recorded and sampled. Among tillage treatments, the greatest runoff, as a percentage of precipitation, occurred from the disked watersheds (11.5% yr^{-1}) and the greatest number of events (37 yr^{-1}) occurred from the no-till watersheds. The least amount of runoff, as a percentage of precipitation (6.6% yr^{-1}), and the fewest events (13 yr^{-1}) occurred from the chisel-tilled watersheds.

Herbicide Transport

Herbicide losses varied considerably among watersheds and years as a result of variation in rainfall timing and amounts. As a percentage of application, average annual losses were highest for all four herbicides for the no-till watersheds and were generally similar for chisel-tilled and reduced-input treatments (Table 2). The highest annual loss observed for any of the herbicides was 4.71% and occurred when atrazine was applied to the no-till Watershed 118 in 1995. Most of this loss (78%) was the result of a single runoff event that began on 18 May, 2 d after herbicide application. Similarly, the greatest losses of alachlor (1.02%) and linuron (2.16%) were the result of the same event on the same watershed, with the 18 May 1995 event contributing to 71% of the yearly alachlor loss and 76% of the yearly linuron loss. The greatest metribuzin loss (2.31%) was noted on the reduced-input Watershed 111 in 1997 as a consequence of a storm that began 13 d after application, resulting in 84% of the annual loss.

Alachlor was applied each time corn or soybean was grown and was detected in runoff in all of these crop years on all watersheds. Additionally, alachlor was detected in 4 out of the 9 yr in which wheat was grown and alachlor was not applied. In contrast, although atrazine was applied only in corn years, it was detected in runoff in all years, including the 9 yr in which wheat was grown on the reduced-input watersheds. Like atrazine, linuron was only applied during the corn years; however, it was only detected in runoff in 4 of the 27 soybean yr and then in only small amounts. It was only detected in one of the wheat years (Watershed 127 in 1999) and this was as the result of a single runoff event in July and may have been due to spray drift, deposition in rainfall, or sample contamination. Metribuzin was only applied during the soybean years and was only detected in runoff in 5 of the 27 corn yr and 1 of the 9 wheat yr and then only in small amounts. The sporadic nature of these detections suggested that they were the result of contamination or deposition in rainfall.

Average alachlor loss when broadcast applied at a half rate on the reduced-input watersheds in corn years (0.11%) was nearly identical to the loss observed when a half-rate application was achieved by banding over the rows in soybean years (0.12%). Thus, there appeared to be no advantage in terms of herbicide losses in surface runoff to banding vs. a reduced-rate application in this comparison. In a plot study, however, Hansen et al. (2001) noted that banding reduced alachlor losses com-

Table 2. Precipitation, number of runoff events and percentage of rainfall, and losses of alachlor, atrazine, linuron, and metribuzin in surface runoff.

Crop year	Crop	Rainfall	Runoff		Alachlor†	Atrazine†	Linuron†	Metribuzin†
		mm	no. of events	% of rainfall	% of applied			
				Watershed 109, Chiseled				
1993	soybean	926	16	0.7	0.0025	0.0010/na	na/nd	0.014
1994	corn	997	3	<0.1	tr	0.0002	tr	na/nd
1995	soybean	865	6	1.5	tr	na/tr	na/nd	tr
1996	corn	1052	8	1.3	0.0011	0.0075	0.0001	na/tr
1997	soybean	918	15	0.2	0.015	0.0007/na	na/nd	0.032
1998	corn	866	8	0.2	0.0006	0.0026	0.0011	na/nd
1999	soybean	912	10	0.1	0.0001	na/tr	na/nd	tr
2000	corn	892	5	0.3	0.0002	0.0002	nd	na/nd
2001	soybean	992	5	0.3	0.0012	0.0001/na	na/nd	0.0010
				Watershed 123, Chiseled				
1993	corn	1007	12	15.0	0.15	0.90	0.46	na/nd
1994	soybean	861	14	5.6	tr	0.0025/na	na/nd	0.0002
1995	corn	1071	25	16.6	0.71	2.49	1.19	na/nd
1996	soybean	960	21	12.2	0.057	0.0033/na	na/nd	0.19
1997	corn	1042	25	16.2	0.80	2.10	0.68	na/nd
1998	soybean	895	17	17.6	0.032	0.028/na	na/nd	0.15
1999	corn	956	8	8.6	0.0068	0.0072	0.0045	na/nd
2000	soybean	854	8	10.1	0.0083	0.0023/na	na/nd	0.0010
2001	corn	1102	21	12.1	0.23	0.40	0.30	0.0005/na
Mean chiseled‡		953	13	6.6	0.11	0.66	0.29	0.04
				Watershed 113, No-till				
1993	soybean	864	24	11.1	0.15	0.044/na	na/nd	0.80
1994	corn	1023	29	3.2	0.0063	0.077	0.015	na/nd
1995	soybean	931	25	5.6	0.068	0.0026/na	na/nd	0.22
1996	corn	1087	35	4.5	0.15	0.44	0.21	na/nd
1997	soybean	959	27	6.4	0.61	0.015/na	na/nd	2.16
1998	corn	893	24	7.3	0.055	0.65	0.19	na/nd
1999	soybean	939	15	3.8	0.0038	0.0019/na	na/nd	0.0056
2000	corn	878	35	5.5	0.14	0.68	0.36	na/nd
2001	soybean	1008	19	3.3	0.44	0.0053	na/tr	0.81
				Watershed 118, No-till				
1993	corn	1025	51	13.8	0.12	1.10	1.04	na/nd
1994	soybean	890	46	5.7	0.035	0.0042/na	0.0005/na	0.22
1995	corn	1116	63	14.0	1.02	4.71	2.16	na/tr
1996	soybean	982	52	8.4	0.38	0.0022/na	na/nd	0.84
1997	corn	1074	46	12.0	0.86	2.72	1.67	na/nd
1998	soybean	925	42	14.6	0.12	0.0052/na	na/nd	0.63
1999	corn	973	37	6.3	0.0076	0.014	0.0059	na/nd
2000	soybean	885	47	9.9	0.53	0.0027/na	na/nd	1.75
2001	corn	1117	47	9.6	0.31	1.17	0.61	na/nd
Mean no-till‡		976	37	8.1	0.28	1.29	0.70	0.83
				Watershed 111, Disked				
1993	corn	887	21	17.7	0.022	1.22	0.43	na/nd
1994	soybean	966	27	7.9	0.0043	0.0059/na	na/nd	0.071
1995	wheat	1091	37	13.1	na/nd	0.0038/na	na/nd	na/nd
1996	corn	887	26	10.6	0.090	0.51	0.044	na/nd
1997	soybean	1051	29	16.6	0.72	0.029/na	na/nd	2.31
1998	wheat	877	24	16.0	na/nd	0.0012/na	na/nd	na/nd
1999	corn	940	14	9.4	0.012	0.0074	0.0009	0.0009/na
2000	soybean	971	21	6.9	0.0089	0.0024/na	na/nd	0.017
2001	wheat	914	19	7.9	0.0060/na	0.0010/na	na/nd	0.013/na
				Watershed 115, Disked				
1993	soybean	1016	26	9.5	0.065	0.011/na	na/nd	0.22
1994	wheat	895	14	1.8	na/nd	na/tr	na/nd	na/nd
1995	corn	1165	37	5.6	0.011	0.47	0.24	na/nd
1996	soybean	928	30	5.4	0.0033	0.0005	na/nd	0.0055
1997	wheat	934	20	4.5	0.0001/na	0.0015/na	na/nd	na/nd
1998	corn	895	19	3.7	0.0066	0.27	0.036	na/nd
1999	soybean	977	23	7.4	0.012	0.0020/na	na/tr	0.011
2000	wheat	840	33	8.4	0.0040/na	0.0005/na	na/nd	na/nd
2001	corn	1050	21	6.0	0.061	0.46	0.14	na/nd
				Watershed, 127 Disked				
1993	wheat	944	38	23.1	0.0022/na	0.0066/na	na/nd	na/nd
1994	corn	1018	46	9.5	0.0020	0.11	0.015	na/nd
1995	soybean	914	51	21.0	0.0001	0.0055/na	na/nd	0.0001
1996	wheat	960	56	9.5	na/nd	0.0018/na	na/nd	na/nd
1997	corn	1042	42	18.0	0.78	4.34	0.85	na/nd
1998	soybean	950	36	22.0	0.045	0.015/na	0.0001/na	0.28
1999	wheat	877	24	17.7	0.025/na	0.0047/na	0.0012/na	na/nd
2000	corn	885	23	13.5	0.039	0.78	0.16	0.0001/na
2001	soybean	1045	49	18.4	0.25	0.0075/na	na/nd	2.04
Mean disked‡		960	30	11.5	0.12	0.92	0.21	0.55

† na = not applied, nd = not detected, tr = trace < 0.0001%. Losses in crop years when the herbicide was detected, but not applied, are based on the rates in the year of application (3.36 kg ha^{-1} alachlor, 2.24 kg ha^{-1} atrazine, and 1.12 kg ha^{-1} linuron in corn years and 3.36 kg ha^{-1} alachlor and 0.38 kg ha^{-1} metribuzin in soybean years with half rates on reduced-input watersheds).

‡ Tillage treatment means for herbicide loss percentages are the means of the amount applied, thus are not numerical averages of the yearly losses.

pared with broadcast application. They attributed this finding to a reduction in runoff volume due to greater between-row weed cover in the banded plots.

The spectrum of weeds controlled by linuron is similar to that of atrazine. Within watersheds and years, linuron losses were always less than atrazine losses (Table 2) and a paired *t*-test for all watersheds and years indicated that these values were significantly different at $P = 0.0024$. Averaged across all tillage treatments and years, linuron loss (0.40%) was less than atrazine loss (0.96%). Furthermore, Gilliom et al. (1999) noted that while atrazine was frequently detected in streams, linuron was rarely detected, which they attributed to differences in the physical and chemical properties of these compounds. Thus, this data further supports the conclusion of Shipitalo et al. (1997) that herbicide loading in surface runoff can be reduced by replacing atrazine with linuron.

Herbicide Concentrations

The highest concentrations of all herbicides were noted in the first few events after application and concentrations declined rapidly with time and subsequent events, as is typically observed in field studies (Wauchope, 1978). The relationship between atrazine concentration and days after application (DAA) was typical of what was observed for all four herbicides (Fig. 1). As can be seen in Fig. 1, the decline in concentration with DAA was similar for all tillage treatments. Unlike the other herbicides, however, atrazine was consistently detected in runoff in the second and third years following application. Since atrazine was reapplied to the chisel-tilled and no-till watersheds every 2 yr, observations of atrazine beyond ~750 DAA were limited to reduced-input watersheds in the 3-yr rotation. For all tillage treatments, most of the 158 events with flow-weighted atrazine concentrations above the 3 μg L^{-1} MCL occurred within the first 100 d after application. In seven instances, however, atrazine concentrations exceeded the MCL around 350 to 400 DAA (Fig. 1). These observations coincided with a slight increase in concentration that occurred at the time of tillage and planting operations. A similar increase was also noted with the second round of tillage and planting operations at 750 to

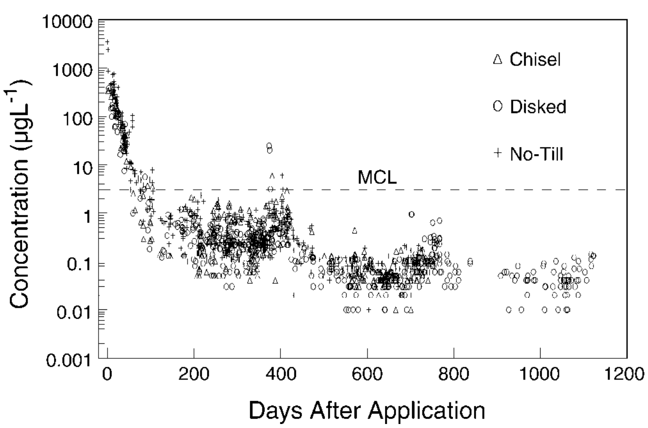


Fig. 1. Relationship of flow-weighted atrazine concentration in individual runoff events to days after application for all seven watersheds for the 9-yr period. MCL is maximum contaminant level.

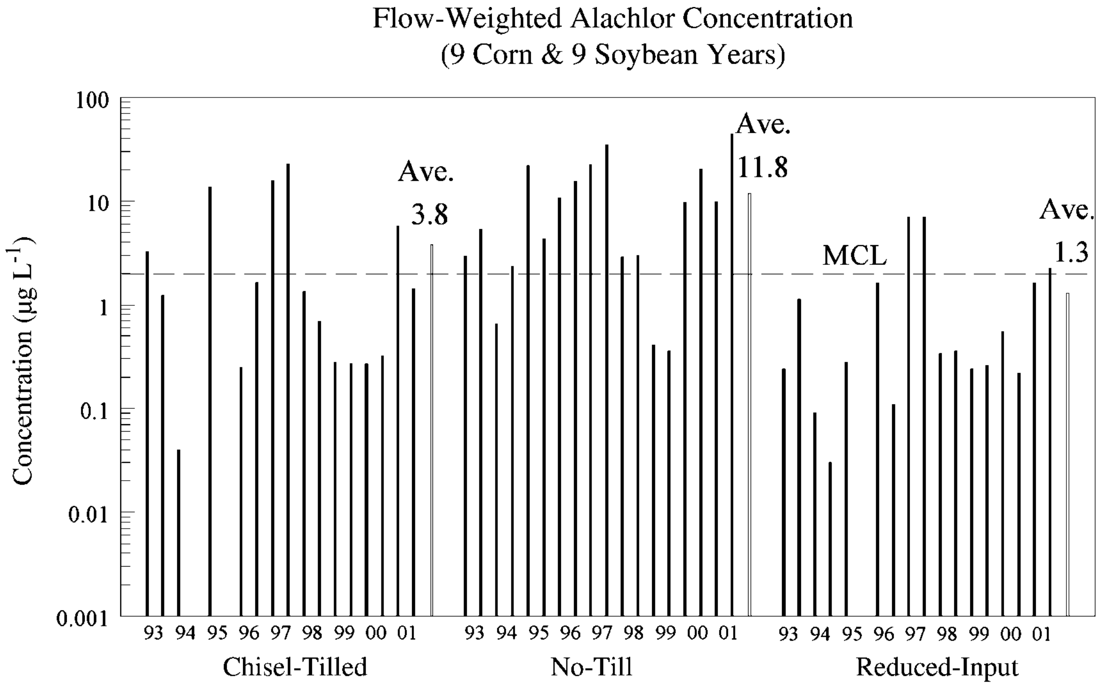
800 DAA. These observations suggested that soil disturbance, contamination due to deposition in rainfall, or both contributed to the slight increase in atrazine concentrations in surface runoff in the spring. Goolsby et al. (1997) reported that rainfall in the midwestern and northeastern USA frequently contains trace concentrations of herbicides in the spring, with atrazine and alachlor being the most commonly detected materials. Similarly, pesticide concentrations in rainfall in Germany have been found to exceed drinking water standards (Hüskes and Levsen, 1997).

Yearly, flow-weighted herbicide concentrations averaged for the 9-yr period were highest for the no-till treatment (Fig. 2). The highest annual concentrations (alachlor in 2001, 44.5 μg L^{-1}; atrazine in 1995, 67.7 μg L^{-1}; linuron in 1995, 15.5 μg L^{-1}; metribuzin in 1997, 13.6 μg L^{-1}) were also noted on the no-till watersheds (Fig. 2). Thus, both herbicide transport (Table 2) and concentrations were greater with the no-till management practice than with the other two tillage treatments. The yearly, flow-weighted atrazine concentrations from all watersheds exceeded the 3 μg L^{-1} MCL in most corn years, even when applied at a half rate to the reduced-input watersheds. Similarly, flow-weighted concentrations of alachlor exceeded its MCL of 2 μg L^{-1} for 15 out of 18 watershed years for the no-till treatment, 5 out of 18 yr for chisel-tilled, and 3 out of 18 yr with the reduced-input treatment (Fig. 2). Yearly, flow-weighted metribuzin concentrations were well below its health advisory level (HAL) of 200 μg L^{-1}. Linuron has no established MCL or HAL.

Extreme Events

During the 9 yr of the study an average of almost 200 separate precipitation events were recorded each year at the NAEW. Most of these nearly 1800 events did not result in runoff. The timing of the runoff-producing precipitation events relative to herbicide application, however, was critical in determining the herbicide losses from the watersheds. The single largest transport event accounted for an average of 42% of the alachlor and atrazine losses from all seven watersheds (Table 3). These percentages were slightly higher but not significantly different ($P = 0.05$) for linuron (51%) and metribuzin (54%), which are less persistent than alachlor and atrazine. These were not necessarily events that produced large volumes of runoff, as indicated by the runoff volume rankings in Table 3. In all cases, these events occurred within 50 DAA, except for atrazine on the chisel-tilled Watershed 109 (Table 3). Of the seven watersheds, Watershed 109 had the fewest runoff events and the lowest average percentage herbicide loss (Table 2), and the 4 Feb. 1996 runoff event that transported the largest amount of atrazine was the second largest event by volume during the 9-yr period for Watershed 109.

The cumulative transport attributable to the top five transport events further highlights the fact that a few events were responsible for most of the herbicide loss (Table 3). These events transported an average of 86% of the herbicide (range 60–99%). In this case, analysis of variance and LSD revealed that the average loss of the



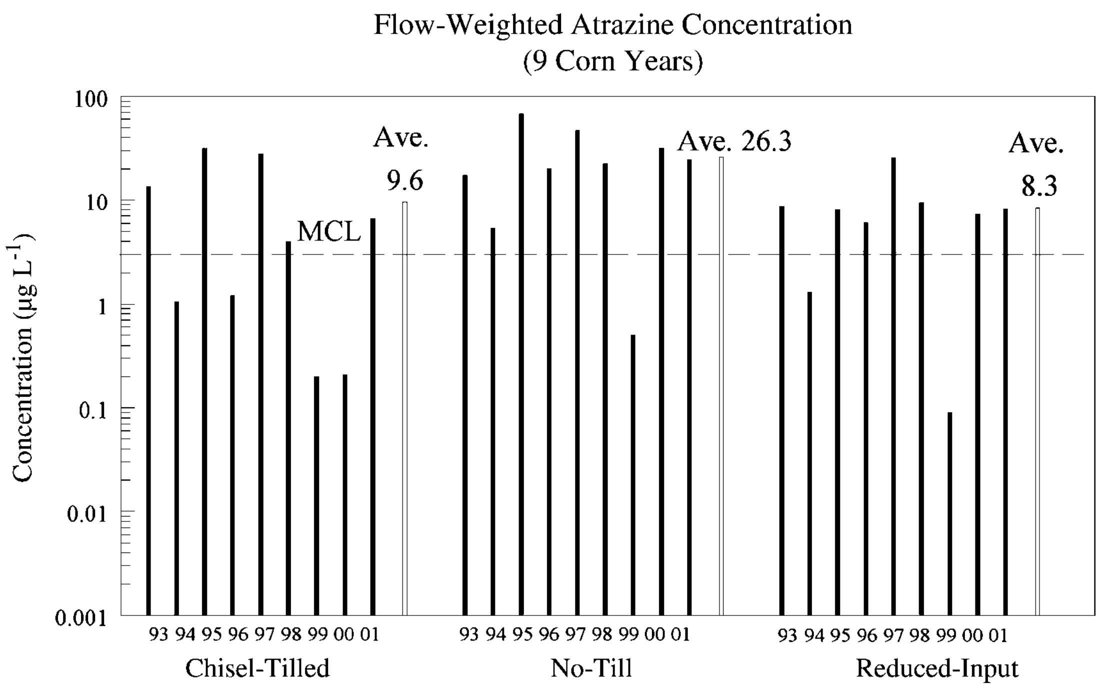


Fig. 2. **Continued on next page.**

less persistent herbicide metribuzin (92%) was significantly greater ($P = 0.05$) than that of alachlor (78%) and atrazine (85%). The average loss of linuron (89%) was only significantly different from that of alachlor. All but 9 of these 135 events occurred within 100 DAA, with six of the nine exceptions occurring on the low-runoff-producing Watershed 109 and the other three events responsible for 2% or less of the herbicide transport. The cumulative percentage losses for the two no-till watersheds were consistently lower than for the watersheds in the other tillage treatments. This probably reflected the fact that the watersheds under the no-till treatment had the largest average number of runoff events of the three management systems (Table 2).

Thus, unlike erosion where a few large storms and the large runoff volumes they can generate result in most of the sediment loss (Edwards and Owens, 1991; Langdale et al., 1992; Larson et al., 1997), herbicide losses were much more dependant on the timing of the storms relative to herbicide application, hence herbicide concentration, than runoff volume. This dependence of transport on concentration can be illustrated by

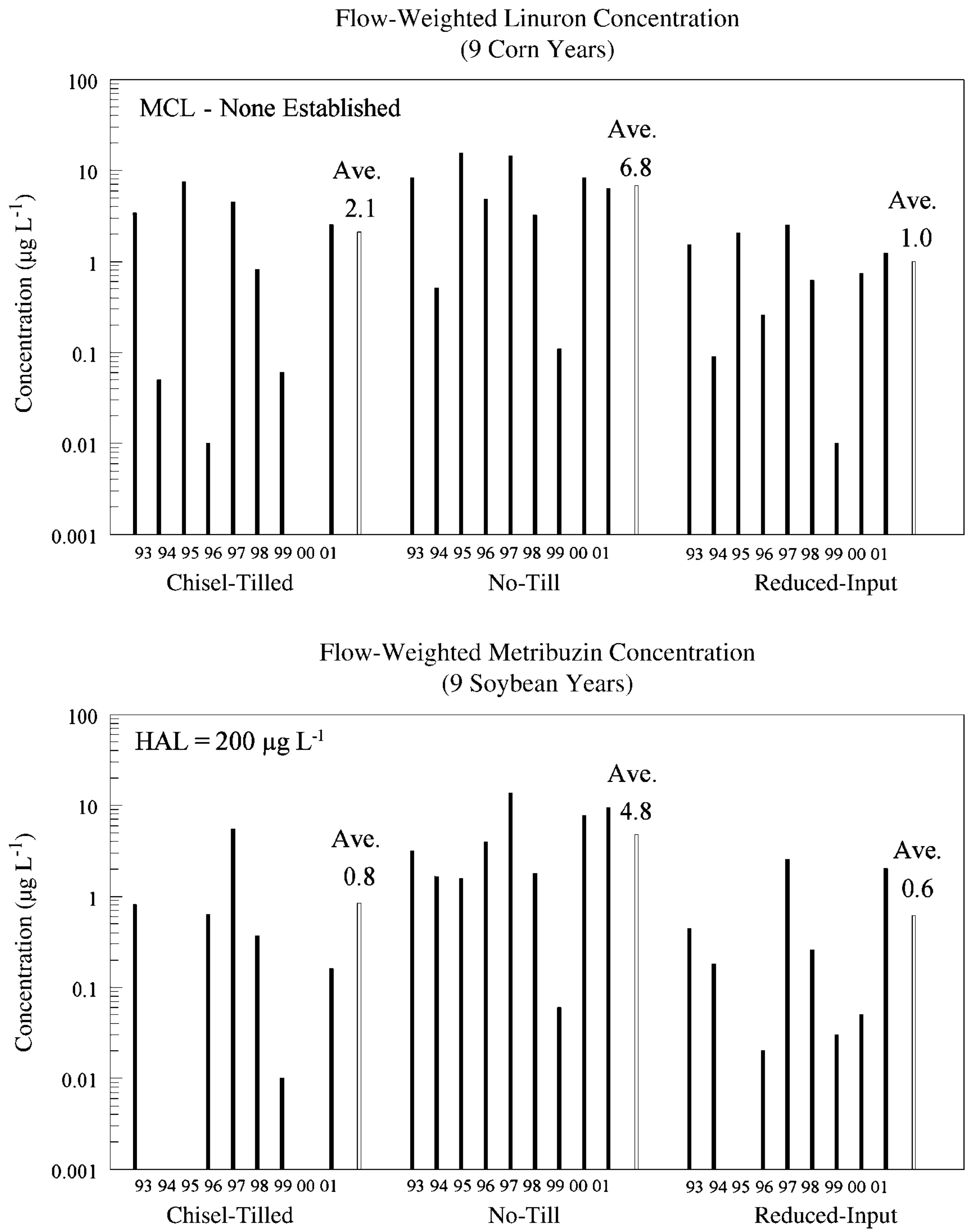


Fig. 2. Yearly, flow-weighted, average concentrations of alachlor, atrazine, linuron, and metribuzin in runoff from the chisel-tilled, no-till, and reduced-input watersheds. Since alachlor was applied in corn and soybean crop years, there are two averages for each year for this herbicide, but only one average per year for the others. HAL is health advisory level, MCL is maximum contaminant level.

examining the range of concentrations observed. The highest flow-weighted atrazine concentration noted was 3452 $\mu g\ L^{-1}$ on 8 May 1997 for runoff that occurred on the afternoon following application to no-till Watershed 118. This is more than 1000-fold higher than the atrazine MCL and five orders of magnitude greater than the detection limit. Thus, 1 mm of runoff at this concentration can transport more atrazine than 100 m of runoff with atrazine concentration at the detection limit. Similarly, it would take more than 1000 L of atrazine-free water to dilute 1 L of runoff at this concentration to below the MCL. This same event produced the highest flow-weighted linuron concentration of 664 $\mu g\ L^{-1}$. The highest flow-weighted alachlor concentration was 1424 $\mu g\ L^{-1}$ on 23 May 2000 for runoff that occurred the day after application to soybean on Watershed 118. This is 700-fold higher than the MCL for alachlor. This same event produced the highest flow-weighted metribuzin

Table 3. Percentage of total herbicide loss due to the top five transport events during the nine crop years.

	Chiseled		No-till		Disked		
Rank	Watershed 109	Watershed 123	Watershed 113	Watershed 118	Watershed 111	Watershed 115	Watershed 127
	%†						
			Alachlor				
1	50 (7/21)	34 (25/3)	22 (28/10)	21 (29/2)	76 (28/13)	31 (4/50)	61 (30/17)
2	22 (20/19)	30 (31/17)	17 (6/19)	18 (22/17)	10 (105/3)	16 (70/11)	18 (28/10)
3	11 (10/31)	7 (11/35)	9 (8/21)	8 (56/6)	3 (6/37)	12 (57/12)	3 (16/38)
4	5 (6/75)	5 (77/19)	7 (61/4)	6 (32/19)	3 (21/35)	7 (5/76)	3 (32/39)
5	3 (2/256)	4 (9/41)	6 (36/16)	6 (131/2)	2 (12/35)	7 (25/10)	2 (4/75)
Total	92	80	61	60	95	73	87
			Atrazine				
1	34 (2/256)	36 (25/3)	27 (36/16)	38 (29/2)	64 (12/35)	37 (25/10)	56 (30/17)
2	15 (24/41)	21 (31/17)	17 (7/40)	17 (22/17)	27 (105/3)	22 (11/36)	14 (69/11)
3	14 (4/245)	13 (11/35)	15 (51/25)	9 (32/19)	2 (113/46)	18 (57/12)	10 (15/41)
4	10 (5/248)	6 (9/41)	11 (58/14)	6 (8/35)	2 (1/255)	15 (70/11)	9 (32/39)
5	7 (10/404)	5 (24/39)	6 (91/15)	4 (91/8)	1 (6/37)	3 (5/76)	5 (102/24)
Total	80	81	75	74	95	95	94
			Linuron				
1	56 (24/41)	41 (25/3)	35 (36/16)	30 (29/4)	90 (12/35)	57 (25/10)	45 (30/17)
2	36 (30/40)	16 (11/35)	15 (7/40)	20 (22/17)	9 (105/3)	19 (70/11)	16 (15/41)
3	5 (59/31)	13 (31/17)	13 (58/14)	11 (8/35)	1 (113/46)	14 (57/12)	16 (32/39)
4	2 (36/83)	6 (77/19)	8 (51/25)	6 (32/19)	<1 (86/218)	9 (11/36)	15 (69/11)
5	1 (49/104)	6 (9/41)	6 (99/12)	4 (64/20)	<1 (72/222)	1 (112/23)	4 (102/24)
Total	99	83	77	71	99	99	96
			Metribuzin				
1	50 (7/21)	42 (16/42)	21 (6/19)	24 (131/2)	81 (28/13)	76 (4/50)	85 (28/10)
2	30 (10/31)	30 (99/8)	16 (28/10)	22 (56/6)	6 (6/37)	8 (53/49)	8 (16/38)
3	17 (20/19)	25 (115/6)	15 (61/4)	12 (77/5)	5 (21/35)	7 (151/29)	3 (181/23)
4	2 (6/75)	2 (102/44)	13 (8/21)	10 (57/27)	4 (102/20)	2 (89/50)	2 (4/75)
5	<1 (38/43)	1 (109/6)	12 (3/32)	5 (13/42)	3 (75/47)	1 (116/51)	1 (120/22)
Total	99	99	78	73	99	94	99

† Values in parentheses are event size, ranked by runoff volume, followed by number of days after herbicide application that runoff occurred.

concentration of 562 μg L^{-1}, which is nearly three times greater than the 200 μg L^{-1} HAL for this herbicide.

DISCUSSION

During the 9-yr period investigated (63 watershed years) losses of the four herbicides averaged 1.29% or less of the amount applied and never exceeded 5% in an individual year. Thus, the losses were within the ranges typically reported for field studies (Wauchope, 1978). For the watersheds investigated, however, both flow-weighted yearly average concentrations and average herbicides losses were greater for no-till than for the watersheds in the other two tillage treatments. Average herbicide losses as a percentage of application from the reduced-input practice were 1.4 to 3.3 times lower than those from the no-till watersheds, despite the fact that runoff, as a percentage of rainfall, was 1.4 times greater from the reduced-input watersheds (Table 2). This suggested that although no-till crop production can increase infiltration and reduce runoff, it can result in increased herbicide losses and concentrations compared with instances were greater amounts of tillage are used. This finding is in contrast to some other field studies under natural rainfall in which the reduction in runoff volume from soils under reduced tillage was sufficient to offset the higher herbicide concentrations noted with reduced tillage compared with tilled soils (Fawcett et al., 1994; Holland, 2004; Locke and Bryson, 1997).

Although the watersheds under the reduced-input practice had lower herbicide transport percentages than the no-till watersheds, the lowest losses for all herbicides (except linuron) were observed from the chisel-tilled watersheds. Nevertheless, since the herbicide application rates were half those of the chisel-tilled, either due to banding or reduced-rate applications, the yearly flow-weighted concentrations were lower for all herbicides for the reduced-input watersheds (Fig. 2). Regardless of tillage practice or reduced-rate applications, however, the yearly flow-weighted atrazine concentrations frequently exceeded the regulatory limits for drinking water in the year of application. Likewise, flow-weighted alachlor concentrations from all tillage treatments exceeded its MCL in some years, although not as frequently as observed with atrazine. Thus, substitution of cultivation for some of the herbicide input used with conservation tillage reduced herbicide transport compared with no-till, but concentrations of atrazine and alachlor were still high enough to remain a concern.

Increased tillage associated with the reduced-input practice also carries a greater risk of soil and crop yield loss. Previous research on these same watersheds indicated that the average soil losses from all tillage practices were well below the tolerance level of 7.8 Mg ha^{-1} yr^{-1}, but the average soil loss from the reduced-input watersheds (1.0 Mg ha^{-1} yr^{-1}) was twice that from no-till watersheds in which a row crop was produced each year rather than only 2 out of 3 yr (Shipitalo and Edwards, 1998). Additionally, infrequent, severe storms caused most of the soil loss from these watersheds. Siegrist et al. (1998) also noted that tillage-based crop production did not offer sufficient protection against erosion during severe storms. Furthermore, crop yields were more variable from the reduced-input than from the no-till and chisel-till watersheds, partially due to the inability to cultivate in a timely manner due to weather conditions (Shipitalo and Edwards, 1998). In a study comparing weed control with herbicides vs. cultivation, Heydel et al. (1999) also noted that corn yields were lower with cultivation alone due to timing problems and difficulty controlling in-row weeds.

For all of the watersheds and tillage practices, a few events, usually within 100 DAA, caused most of the herbicide loss. During this study, the top five transport events for each herbicide and watershed accounted for 60 to 99% of the herbicide losses for the 9-yr period. These events were not necessarily the result of large storms that produced large runoff volumes, but generally were runoff events that had high herbicide concentrations. Thus, to reduce yearly flow-weighted herbicide concentrations to acceptable levels, management practices or control measures must be devised that reduce these herbicide concentrations from these extreme events to be effective. Furthermore, this highlights the fact that to properly sample or model herbicide loss in surface runoff, sampling strategies and transport models must accurately capture the contribution of these events. If these events are missed, herbicide losses will be grossly underestimated as most other storms and runoff events are inconsequential in terms of herbicide transport. As with soil loss, long-term studies are needed to fully evaluate the effects of conservation tillage practices on herbicide losses in surface runoff.

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